ACP review by Annonymous referee 1:

MS title: Molecular distribution and compound-specific stable carbon isotopic composition of dicarboxylic acids, oxocarboxylic acids, and α-dicarbonyls in PM2.5 from Beijing, China

Organic aerosols (OAs) account for major fraction of atmospheric particulate matter and also ubiquitous in nature. Among the OAs, the dicarboxylic acid and related polar compounds are one such widely studied chemical species that provide useful information about the relative significance of anthropogenic versus natural source contributions as well as primary emissions vs. secondary formation processes. In this context, combining the molecular distributions, concentrations, diagnostic mass ratios, air mass back trajectories and their stable carbon isotopic composition from this kind of studies are helpful in improving our current understanding of the complex nature of OAs. Therefore, the study is most relevant and publishable in ACP after a major revision.

I feel that conclusions are more clear and focussed than the most of the text part of this MS. The comparison of mass ratios among seasons are too vague. This should be supported by the statistical analysis such as ANOVA. To me, comparison of mean and sd of mass ratios of dicarboxylic acids among seasons appear to be insignificant for this study. In order to truly appreciate the relative significance of various source emissions (biogenic vs. anthropogenic) based on mass ratios of dicarboxylic acids and other related polar compounds, I strongly recommend the authors to evaluate their seasonal datasets using a statistical test (e.g, ANOVA). I see that there is a missing link in terms of attributing the stable carbon isotopic composition of dicarboxylic acids' with source contributions. For example, how the lowest $\delta^{13}C$ value of terephthalic acid (~-33.5‰) in winter indicates that it is emitted from plastic waste burning. Why not in other seasons? Is the plastic waste burning over Beijing is common only winter?

Another important issue is Section 3.6, 3.7 and 3.8: comparison of $\delta^{13}C$ of diacids and other compounds measured here makes this study unique due to year round sampling and comparing seasons. However, all these sections are bit complicated to follow/read. Since the East Asian outflow influences the chemical composition of organic aerosols during winter and spring, it is relevant to compare the diacid $\delta^{13}C$ values from this study with other sites/studies during this period only. No need to include autumn and summer. Therefore, I suggest authors to combine the winter

and spring data sets and use the median values to compare with the other sites in E. Asia (e.g. Sapporo, Gosan & cruises).

My other comments are as follows:

Line 35-37: The sentence is difficult to follow. Please rewrite.

Line 38-40: Correlations of some oxocarboxylic acids and a-dicarbonyls with nss-K+, how significant these are? Mention clearly what is correlated with what? Some oxocarboxylic acids are not specific!

Line 188-190: What is the reason that oxalic acid concentration is found to be highest in autumn and lowest in winter? Similarly, What causes the difference in the seasonality for the relative abundances of oxalic acid? Why is it maximum in summer? Explain/suggest.

Line 192: Update the references with a recent review.

Line 195 to 197. Authors need to provide, why there exist differences in the molecular distribution of measured water-soluble organic compounds among seasons and why do they show different patterns for e.g., why the third most abundant compound is glyoxylic acid in cold period and malonic acid in warmer period?.

Line 199-202: The sentence is not clear. What is single dicarboxylic acid?

Line 203: I am confused with subheading seasonal variability. Authors have already mentioned about differences in the molecular distributions of dicarboxylic acid among seasons already in the previous section. This section has to combine with the section 3.1.

Line 209: abbreviate C_9

Line 204-213: The seasonal trends were attributed to different emissions. This is not enough. Explain what source emissions might contribute for each type and also justify why you think this is the only possibility?

Line 214: Why the total diacid concentrations are the highest in autumn and why it is lowest in winter? Explain.

Line 216: Why Beijing dataset has to be compared with Tanzania, Africa? Both are different settings? Compare with polluted atmosphere with another city in S. Asia or E. Asia. Given the

diverse geographical locations, comparison with only one or two sites cannot be acceptable. Please compare or provide a table and discuss how different or similar this study site with those documented from other cities in China and India.

Line 223-230: After discussing the sources of oxalic acid, why there is a sudden jump to malonic acid data from this study. What about oxalic acid? If it is not important why authors are describing so much about its sources here. Connect here with their formation in different seasons. What are the different sources of oxalic acid, causing this variability through sampling period?

Line 231: Why malonic acid is highest in autumn?

Line 231-234: The connectivity between lines or sentences is missing. Why suddenly succinic acid to malonic acid ratio after mentioning the seasonal variability of malonic acid? What about the seasonal variability of succinic acid? Instead of picking up each compound measured and discussing its seasonality, I suggest authors to briefly summarize or infer logically the possible formation pathways of observed abundant compounds.

Line 231-235: Authors attributed the relative dominance of succinic acid over malonic acid as the major contribution from primary emissions to dicarboxylic acids measured here. Although this could be possible, however, one cannot rule about the transport during each season. So if you see the air mass back trajectories at the receptor site, then this inference based on C4/C3 has certain uncertainty or bias. So you need to mention this in the MS.

Line 235: The diurnal variation tendency of C2?? Is it diurnal or daily variability?

Line 255-257: Why the correlation of azelaic acid (C9) with K+ and Cl- solely attributed to coal burning? Why not biomass burning?

Line 269-271: According to authors “The predominance of terephthalic acid over phthalic acid observed in this study is in contrast with those reported by Ho et al., “. Is it due to variability in the sources or increase plastic waste burning is increasing. Comment on this.

Line 277-278: Provide a reference for the argument that monocarboxylic acids are photochemically oxidized & form dicarboxylic acid. Why authors think it is relevant here rather than direct emissions or other sources.

Line 281: the sentence is not clear.

Line 290–292: These sentences are not clear. You can combine into one as "ωC_2 and Pyr is more abundant in cold seasons (Table 1) and correlated with K^+ and Cl^-". What is the common combustion source, mention it?

Line 326-328: I don't follow the comparison with the Central Himalayan aerosols as well as the logic of the statement. rewrite.

Line 333-339: In urban Beijing, how can authors assume that succinic acid formation forms the photooxidation of unsaturated fatty acids? What about the photochemical oxidation of adipic acid, which is a product of cyclic olefins with oxidants in and around the city? Why not is C4 derived from anthropogenic emissions such as fossil fuel combustion, vehicular emissions in Beijing? The linear relationship between C2/Tot (or relative abundance of oxalic acid in total diacid mass) and the C2/C4 just indicate that oxalic acid has a significant contribution from or formed from the photochemical oxidation of succinic acid, not more than that. So authors need to dilute their emphasis on source attribution directly based on a linear relationship. If still, authors think that succinic acid might have produced from the photochemical breakdown of higher homologues of dicarboxylic acids from the biogenic unsaturated fatty acids, they should the linear relationships with oleic acid and azelaic acid first and then lower homologues of dicarboxylic acids with azelaic acid. I suggest authors think and rewrite along these lines.

Line 335: Authors need to provide a proper reference for invoking contribution of emissions from the phytoplankton in remote oceans (update the reference with diacid review, doi: 10.1016/j.atmosres.2015.11.018 and others cited in).

Line 340-344 and 345-346 is missing. Connect these two as "We, therefore, would like to investigate the significance of these formation pathways by examining the interrelationships between…"

Line 347: correct the sentence as "in all seasons except winter"

Line 352-353: how the negative correlation between oxalic to glyoxylic acid mass ratio and the relative abundance of oxalic acid in summer demonstrate that C_2, ωC_2, Pyr and Gly are from biomass burning emissions? Elaborate further.

Line 361: provide a reference that C_3/C_4 is a good indicator for dicarboxylic acid contribution from primary emissions vs. secondary formation process.

Line 366: correct the sentence as “throughout the sampling year”

Line 367-368. I couldn't find any difference between the two statements.

Line 376-377: Confusing!. State clearly that the direct emissions from localized sources in Beijing contributed to atmospheric dicarboxylic acids.

Line 380-384: I understand for the summer season that Ph might have a contribution from photochemical oxidation of PAHs. What is the reason for its higher abundance in winter season?

Line 396-398: As stated in Line 385, if both adipic acid (C6) and phthalic acid (Ph) are produced from the photochemical oxidation of cyclic olefins, why C6/C9 is lowest in winter and whereas Ph/C9 is highest in winter. Perhaps both could have been produced by different sources. That is the reason why comparing seasonal means directly can yield erroneous interpretations. May be the seasonal averages are not significantly different.

Line 410-414: I am not able to follow the comparison of ratios. Authors need to evaluate the differences in the seasonal means using ANOVA.

Why not authors use PMF other than PCA for the source apportionment in this study, like their previous publications?

Section 3,4: I do not understand the title of this subheading. Already authors made a comparison in the previous section. Then why suddenly there is another section on this?

Line 519-523: I do not follow the logic here. How authors drew their conclusion that d13C of C9 indicate that azelaic acid is from biomass burning in surrounding areas?

Line 534-535: How the lowest $\delta^{13}C$ value of terephthalic acid (~-33.5‰) indicates that it is emitted from plastic waste burning that too in winter. Why not in other seasons? Is the plastic waste burning over Beijing is common only winter. Line 534-535 and the next sentence are not connected. The reference cited is the work related to S. Asia. How about the conditions in E. Asia? Is the plastic waste burning is relevant for the study site? If so, please state it.

Line 538: What major compounds? Be specific (diacids, oxoacids or a-dicarbonyls or what you are referring to).

Line 540: The decreasing trend in $d^{13}C$ of C5 to C9 is not obvious from the Figure 6 for all seasons (see for e.g., summer, panel d).

Line 542-544: given the overlap of the box widths for oxalic, malonic and succinic acids, I wonder whether the 13C enrichment for these compounds is significantly different among seasons.

The scale in Figure 6 is most difficult to compare between seasons. I suggest authors keep the same scale and then discuss the differences.

Figure 8: I do not follow the caption. What are the concentrations plotted on the x-axis.